ULTRAVIOLET ABSORPTION SPECTRA OF ORTHO-AND PARA TOLUNITRILE IN VAPOUR, LIQUID AND SOLID STATES*

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ABSTRACT. The absorption spectra of thin films of *o*-and *p*-tolunitrile in the liquid and the solid states at low temperatures have been studied and the results have been compared with those for the vapour state and for solutions of these substances. Absorption spectra of the substances in the vapour state have also been reinvestigated and the bands have been reclassified. In the liquid state *o*-tolunitrile gives five broad bands with the 0,0 band at 35055 cm^{-1}, while in the vapour state the 0,0 band is at 35780 cm^{-1} and in the solid state at $-180°C$ the bands become sharper and the 0,0 band shifts to 34841 cm^{-1}. In the case of *p*-tolunitrile in the liquid phase seven broad bands are obtained with the 0,0 band at 35771 cm^{-1}, while the 0,0 band due to the vapour is at 36208 cm^{-1}. In the solid state the substance gives nine bands with the 0,0 band at 35752 cm^{-1}. Thus major change in the bands occurs with the liquefaction of vapours, the 0,0 band shifting towards longer wavelengths in both the cases. Such a shift may be due to association of molecules in the liquid state. With solidification and lowering of temperature to $-180°C$, the 0,0 band shifts further towards longer wavelengths in the case of ortho compound but no such change takes place in the case of the para compound. It is concluded that the shift observed with solidification of the ortho compound may be due to larger dipole moment of this molecule than that of the para compound.

INTRODUCTION

The ultraviolet absorption spectra of toluene ($C_6H_5CH_3$) in the liquid and the solid states were investigated by Swamy (1951). The influence of change of state on the electronic energy levels of the molecule is evident from the presence of only one band in the solid state at $-180°C$, the other bands of the liquid state merging into one another. Similar investigations were carried out on the ultraviolet absorption spectra of many disubstituted benzenes in the solid state by Swamy (1952,1953). In the case of *o*-, *p*-xylene at $-180°C$ he observed some new bands which were not observed in the case of the liquid. These bands could be assigned to vibration frequencies of the molecule. In the case of ortho dichlorobenzene the excited state electronic energy level was found to split up into three components with solidification and lowering of temperature to $-180°C$ but the para compound did not show this effect. Such splitting was observed also in the case of chloro and bromotoleune except the para compounds.

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Aromatic nitriles contain C≡N group and it is not known whether the intermolecular field in the solid state has large influence on the ultraviolet absorption spectra of these compounds. Further it would be interesting to compare such influence with that observed in the case of other substituted toluenes and to find out whether the changes in the absorption spectra with solidification of the liquids depend on the relative positions of the substituents as in the case of halogen substituted toluenes. The present investigation was, therefore, undertaken to study the ultraviolet absorption spectra of ortho and para tolunitrile ($CNC_6H_4CH_3$) in the solid state at $-180°C$ to compare the results with those observed for the liquid and vapour states of the substances. The absorption spectra of these substances in the vapour state have also been reinvestigated in order to compare the results with those for the liquid state as the bands reported by Acly (1928) were not properly classified by him. The bands observed in the case of vapours have been reclassified in the present investigation

EXPERIMENTAL

The liquids ortho and para tolunitrile supplied by Fisher Scientific Co. (U.S.A.), were distilled four times under reduced pressure before being introduced in the cell. The films of ortho and para tolunitrile that produced absorption bands had a thickness of only a few microns. The absorption spectra of ortho and para tolunitrile in the vapour state were photographed using an absorption tube of length 50 cm and 14 mm diameter, quartz windows being cemented to the tube with Araldite. For studying the absorption at low temperatures, the brass frame containing the cell with the liquid was suspended in a Dewar vessel of fused silica containing some liquid oxygen. The lower portion of the brass frame was kept immersed in the liquid oxygen to solidify the substance. Liquid oxygen was replenished from time to time to keep it at a proper level in the vessel. The upward drift of cold air prevented the condensation of water vapour on the surfaces of quartz plates. The beam of light coming from the hydrogen discharge tube was made parallel with a quartz lens and the cell was placed in the path of the parallel beam. The transmitted light was focussed on the slit by a second quartz lens. An exposure of about an hour was necessary to record the absorption spectrum of the solid.

A hydrogen discharge tube running at 3 K.V. served as the source of continuous spectrum. Spectrograms were taken on Ilford HP 3 films with a Hilger E 1 quartz spectrograph having a dispersion of 3 A.U. per mm. in the region 2600A°. An exposure of 15 minutes was required to record the spectra of liquids and in the case of vapour the exposure was one and half hour. Iron arc was photographed on each spectrogram as comparison. Microphotometric records were obtained with a self recording microphotometer supplied by Kipp and Zonen. The frequencies of the bands were measured from these microphotometric records in which the record of two known iron lines were taken as reference lines.

RESULTS

The spectrograms of the vapour state are reproduced in Plate XI.

The microphotometric records of the spectrograms due to the solid and liquid states are given in figures 1 and 2. The frequencies of the bands are given in

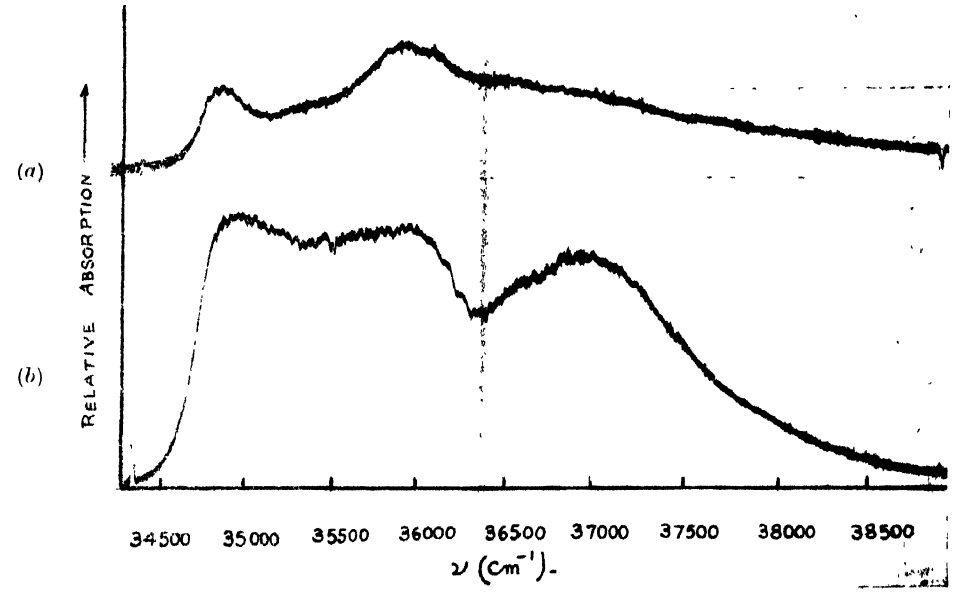


Fig. 1. Microphotometric records of the ultraviolet absorption spectra of ortho tolunitrile.
Curve (*a*) Solid at 180°C, Curve (*b*) Liquid at 32°C

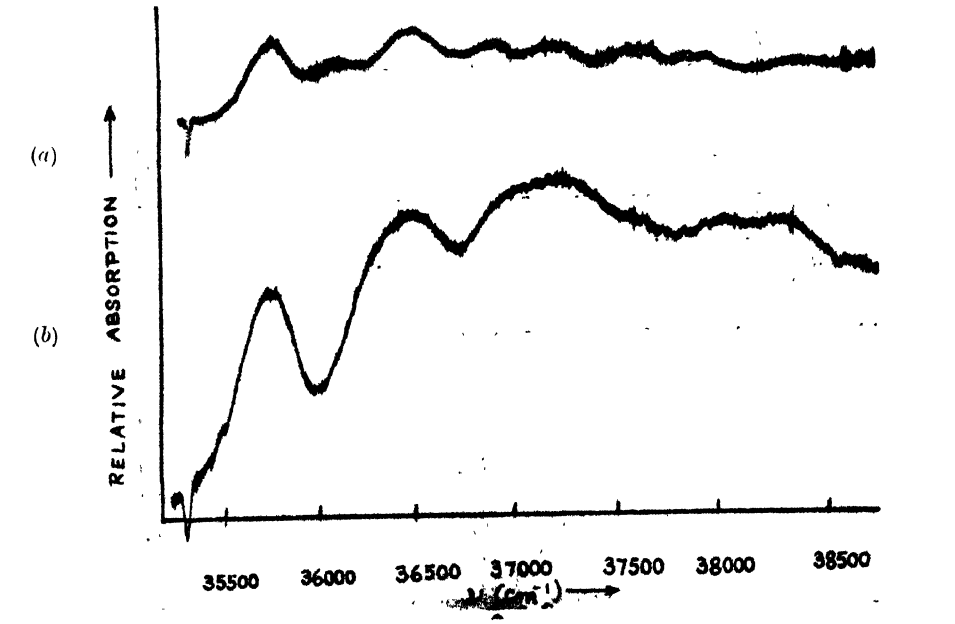


Fig. 2. Microphotometric records of the ultraviolet absorption spectra of para tolunitrile.
Curve (*a*) Solid at −180°C, Curve (*b*) Liquid at 34°C.

Tables I, II, III, IV with approximate relative intensities given as strong, medium, etc. indicated by s, m, etc.

TABLE I

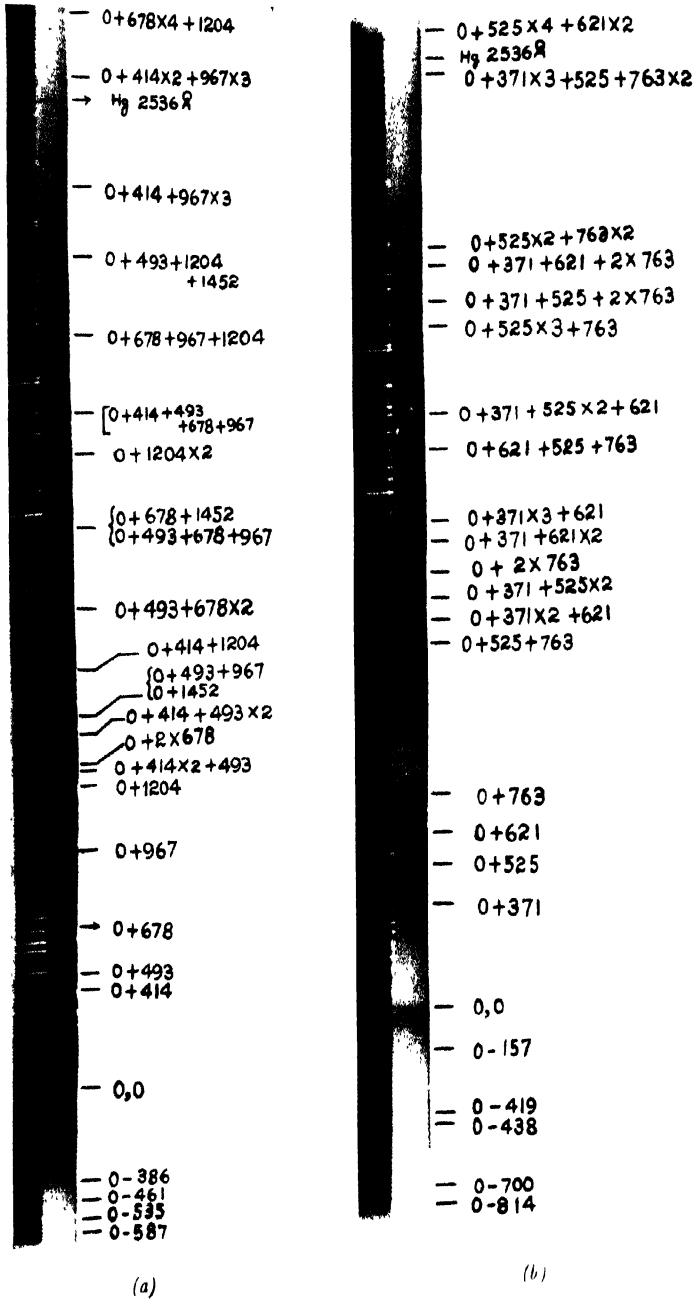
Absorption bands of ortho tolunitrile ($CH_3C_6H_4CN$) in the vapour state (prominent bands)

Wave no. in cm^{-1}	Difference from 0,0 band	Assignment	Wave no. in cm^{-1}	Difference from 0,0 band	Assignment
35193 (w)	−587	0−587	37232(ms)	1452	0+1452 0+493+967
35245(w)	−535	0−535	37397(ms)	1617	0+414+1204
35319(w)	−461	0−461	37632(ms)	1852	0+493+678×2
35394(w)	−386	0−386			
35780(s)	0	0,0	37924(ms)	2144	0+678+1452 0+493+678+967
36194(s)	414	0+414	38182(ms)	2402	0+1204×2
36273(s)	493	0+493	38346(w)	2566	0+414+493+678 +967
36458(s)	678	0+678			
36747(s)	967	0+967	38619(w)	2839	0+678+967+1204
36984(s)	1204	0+1204	38914(w)	3134	0+493+1204+1452
37090(ms)	1310	0+414×2+493	39107(w)	3327	0+414+967×3
37125(ms)	1345	0+2×678	39513(w)	3733	0+414×2+967×3
37191 (ms)	1411	0+414+493×2	39702(w)	3922	0+678×4+1204

TABLE II

Absorption bands of ortho tolunitrile in the liquid and solid states.

Liquid at 32°C			Solid at −180°C		
Wave No. cm^{-1}	Difference from 0,0 band	Assignment	Wave No. cm^{-1}	Difference from 0,0 band	Assignment
35055(s) (broad)	0	0,0	34841(s)	0	0,0
35693(ms) (broad)	638	0+638	35400(W)	559	0+559
			35983(s)	1142	0+1142
36100(s) (broad)	1045	0+1045	36552(w) (broad)	1711	0+559+1142
36726(ms) (broad)	1671	0+638+1045	37114(w) (broad)	2273	0+1142×2
37136(s) (broad)	2081	0+1045×2			



Ultraviolet absorption spectra

(a) Ortho-tolunitrile Vapour at 40°C.

(b) Para-tolunitrile Vapour at 40°C

TABLE III

Absorption bands of para tolunitrile ($CH_3C_6H_4CN$) in the vapour state (prominent bands)

Wave no. in cm^{-1}	Difference from 0,0 band	Assignment	Wave no. in cm	Difference from 0,0 band	Assignment
35394(w)	−814	0−814	37814(ms)	1606	0+371+621×2
35508(w)	−700	0−700	37917(ms)	1709	0+371×3+621
35770(w)	−438	0−438	38133(ms)	1925	0+621+526+763
35789(w)	−419	0−419	38247(ms)	2039	0+371+525×2+621
36051(w)	−157	0−157			
36208(s)	0	0,0	38531(ms)	2323	0+525×3+763
36579(s)	371	0+371	38613(ms)	2405	0+371+525+2×763
36733(s)	525	0+525	38732(ms)	2524	0+371+621+2×763
36829(s)	621	0+621			
36971(s)	763	0+763	38790(w)	2582	0+525×2+763×2
37492(ms)	1284	0+525+763	39373(w)	3165	0+371×3+525+763×2
37558(ms)	1350	0+371×2+621			
37628(ms)	1420	0+371+525×2	39535(w)	3327	0+525×4+621×2
37738(ms)	1530	0+763×2			

TABLE IV

Absorption bands of para tolunitrile ($CH_3C_6H_4CN$) in the liquid and solid states

Liquid at 32°C			Solid at −180°C		
Wave No. cm^{-1}	Difference from 0,0 band	Assignment	Wave No. cm^{-1}	Difference from 0,0 band	Assignment
35771(s) (broad)	0	0,0	35752(s)	0	0,0
			36123(w)	371	0+371
36513(s) (broad)	742	0+742	36492(s)	740	0+740
36953(s) (broad)	1182	0+1182	36948(ms)	1196	0+1196
			37232(ms)	1480	0+740×2
37245(s) (broad)	1574	0+2×742	37612(ms)	1860	0+371+740×2
37684(w)	1913	0+742+1182	37696(ms)	1944	0+740+1196
38133(w)	2362	0+1182×2	37962(w)	2210	0+740×3
38445(w)	2674	0+2×742+1182	38339(w)	2587	0+371+740×3

DISCUSSION

o-Tolunitrile—

Ultraviolet absorption bands of *o*-tolunitrile in the vapour state were reported by Acly (1928) and assignments of the bands made by him according to the following two series

Series I — $35769+(p'-p_0)\,970-50p_0+(q'-q_0)300$

Series II — $35545+(p'-p_0)\,970-50p_0+(q'-q_0)300+(r'-r_0)\,715$

In the present investigation, the intense band at 35780 cm^{-1} is taken as the 0,0 band. On the longer wave length side of this band there are some feeble bands which can be assigned as 0—386, 0—461, 0—535, 0—587, the corresponding frequencies of the Raman spectra of the liquid (Magat, 1936) being 385 cm^{-1}, 457 cm^{-1}, 541 cm^{-1}, 591 cm^{-1}. There are however strong companions on the red side and in the immediate neighbourhood of some of the main band heads. These are probably due to $v\rightarrow v$ transitions. Progressions of excited state frequencies 414, 493, 678, 967 and 1204 cm^{-1} have been observed. An alternative assignment of some of the bands has also been made showing 1452 cm^{-1} as an excited state vibration frequency. This frequency has been observed in the case of *p*-dichlorobenzene by Anno and Matubara (1955).

In the liquid state five bands have been found, the 0, 0 band being at 35055 cm^{-1}. The rest of the bands represent progressions of excited state frequencies 638 cm^{-1}, 1045 cm^{-1} and their combination and harmonics. It is found that 0, 0 band shifts towards longer wavelength side by 725 cm^{-1} with the liquefaction of vapour. Such a shift may be explained on the supposition that strong intermolecular field acting on the molecules in the liquid lowers the excited electronic energy state. The broadness of the bands in the liquid state may be due to fluctuation of the intermolecular field caused by thermal motion of molecules. Three bands in solution have been reported by Purvis (1915) at 35078 cm^{-1}, 35960 cm^{-1} and 37026 cm^{-1}. The first band seems to have shifted very slightly towards the shorter wavelength side from the position of the 0, 0 band in the liquid state. This shows that intermolecular field in the solvent has the same influence on the energy state as that in the case of pure liquid. Frequency differences 882 cm^{-1}, 1948 cm^{-1} observed in the case of the solution are not observed in the case of the vapour or the pure liquid. The excited state vibration frequencies 638 cm^{-1} and 1045 cm^{-1} observed in the case of pure liquid do not agree with those observed in the case of the vapour. When the liquid is solidified and cooled to — 180°C the 0, 0 band shifts to 34841 cm^{-1} and progressions of excited state vibration frequencies 559 cm^{-1} and 1142cm^{-1} are observed. These frequencies again are different from those observed in the case of either the vapour or the liquid. These changes in the excited state vibration frequencies with change of state clearly indicate the influence of intermolecular field on the excited state vibrational energy levels. The changes observed in these frequencies with

solidification further show that when the molecules are oriented regularly in the crystal, the intermolecular field is quite different from that experienced by the molecule in the liquid state.

When these results are compared to those due to chlorotoluenes (Swamy, 1952) it is found that the splitting up of the energy levels with solidification observed in the case of chlorotoluenes does not take place in the case of tolunitriles. Also the shift of the 0, 0 band with solidification is towards the longer wavelength side in the present case but in the case of chlorotoluenes or bromotoluenes the shift is towards the shorter wavelength side. Thus the group C≡N as a substituent has an influence on the energy levels in the excited state which is different from that observed in the case of a halogen atom used as the substituent. These latter atoms seem to bring a drastic change in the energy level in the solid state at low temperatures.

p-Tolunitrile—

The ultraviolet absorption bands of *p*-tolunitrile in the vapour state were reported by Acly (1928) and the bands assigned according to the following two series:

Series I $-36755+(p'-p_0)765-28\,p_0+(q'-q_0)128$

Series II $-37102+(p'\ \ p_0)765\ \ 28p_0+(q'-q_0)128$

Hence in Series I he took 36755 cm^{-1} as the frequency of the 0,0 band. It is observed in the present investigation, however,that there is a band at 36208 cm^{-1} which is not much weaker than the band at 36733 cm^{-1} and the frequency difference is 525 cm^{-1}. if the latter band were taken as the 0,0 band the former would have to be assigned as 0—525 but the population of molecules in excited vibrational state of this frequency cannot be so high. So the band at 36208 cm^{-1} has been taken as the 0,0 band. Some feeble bands observed on the longer wavelength side of the 0,0 band can be assigned as 0—157, 0—438, 0—419, 0—700, 0—814. These correspond to the frequency shifts of 161, 437, 410, 705, 819 cm^{-1} found in the Raman spectra of *p*-tolunitrile (Magat, 1936).

In the liquid state seven broad bands, with the 0,0 band at 35771 cm^{-1}, are given by the substance. The 0,0 band is found to have shifted towards longer wavelength side by 437 cm^{-1} on the liquefaction of vapour. The rest of the bands can be assigned to transitions with progressions of vibration frequencies of 742 cm^{-1} and 1182 cm^{-1}. The shift in the 0,0 band and change in the excited state vibrational frequencies taking place with liquefaction may be due to association of molecules through virtual bands in the liquid. Purvis (1915) studied the absorption spectrum of solution of the substance and reported three bands at 35831 cm^{-1}, 36619 cm^{-1} and 36889 cm^{-1} respectively which can be assigned to frequencies 788 cm^{-1} and 1058 cm^{-1}. The 0,0 band in solution appears to have shifted slightly towards shorter wavelength side from the position of the 0,0 band due to the pure liquid. The excited state vibration frequencies are thus entirely dependent

on the intermolecular field. In the solid state at −180°C the substance yields nine sharp bands with the 0,0 band at 35752 cm^{-1}. This band shifts slightly to-towards longer side with solidification. The other bands can be assigned to transitions involving excited state vibration frequencies 371 cm^{-1}, 740 cm^{-1}, 1196 cm^{-} and their combination and harmonics. It is interesting to note that the frequency of 371 cm^{-1} found in the vapour state which persists even in the case of the solid, is absent in the spectrum due to the liquid phase but it appears in the case of the solid.

It is evident from a comparison of the absorption spectra of ortho and para tolunitrile in different states that in both the cases the major change in the 0,0 band takes place with the liquefaction of vapours and the band shifts to longer wavelength side. When the liquids are frozen, the band shifts further towards longer wavelengths in the case of the ortho compound but practically no such change takes place in the case of the para compound. The larger diple moment of the former molecules is responsible for the shift with solidification.

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